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Isomers of pure  $Fe_{13}$  and icosahedral  $Fe_{12}X$  clusters are studied using the all-electron linear-combination-of-Gaussian-type-orbital (LCGTO) local-density-functional (LDF) methods that allow the spin and geometry of the cluster to be determined self-consistently. The  $Fe_{13}$  ground state is icosahedral. The icosahedral cluster also has the greatest magnetic moment because of increased symmetry-required orbital degeneracy for electrons of different spins. The central atom of the icosahedral iron cluster has been varied to optimize the spin of the cluster.

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## Symmetry and Ferromagnetic Clusters

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### ABSTRACT

Isomers of pure  $\text{Fe}_{13}$  and icosahedral  $\text{Fe}_{12}\text{X}$  clusters are studied using the all-electron linear-combination-of-Gaussian-type-orbital (LCGTO) local-density-functional (LDF) methods that allow the spin and geometry of the cluster to be determined self-consistently. The  $\text{Fe}_{13}$  ground state is icosahedral. The icosahedral cluster also has the greatest magnetic moment because of increased symmetry-required orbital degeneracy for electrons of different spins. The central atom of the icosahedral iron cluster has been varied to optimize the spin of the cluster keeping the orbital contribution to the magnetic moment quenched. Varying the central atom under this constraint can alter the magnetic moment by more than 20%. Similar studies have begun on 55-atom icosahedral iron clusters.

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The Linear-combination-of-Gaussian-type-orbitals (LCGTO)<sup>1</sup> local-density-functional (LDF)<sup>2</sup> ground state geometry of the 13-atom iron cluster has approximate icosahedral ( $I_h$ ) symmetry<sup>3</sup> as does the 13-atom nickel cluster<sup>4</sup>. Zero and low magnetic moment, nontransition-metal elemental 13-atom clusters are also icosahedral if directional bonding is not too important<sup>5-6</sup>. The icosahedral 13-atom cluster has two symmetry-inequivalent sets of atoms, a unique central atom surrounded by twelve symmetry equivalent atoms each occupying the corners of an icosahedron. Thus either of these two sets of atoms can be replaced by sets of atoms of a different element without changing the symmetry of the clusters. This work considers the effect of the identity of the central atom on the stability and magnetic moment of the cluster as a whole, and how this approach can be extended to larger icosahedral clusters that have more symmetry-inequivalent shells, which would afford greater possibilities of alloying within the constraint of icosahedral symmetry. This high symmetry can be used to enhance the magnetic moment of these clusters.

The Gaussian orbital basis set for iron was a 15s/11p/6d primitive basis<sup>7</sup> contracted according to an atomic calculation 3,5/2,3/1,3, where for each orbital angular momentum the first number is the number of lowest-energy atomic orbitals (1s to 3s, etc.) and the second number is the number of most diffuse Gaussians used in the cluster calculations (5 s-type, etc.). Compatible primitive Gaussian basis sets from a handbook<sup>8</sup> were augmented with a single *d* polarization function<sup>9</sup> (*f* polarization functions on transition metal atoms in compact structures lead to numerically singular overlap matrices<sup>4</sup>) and every exponent greater than 10 bohr<sup>-2</sup> contracted. For sulphur this approach lead to a 12s/9p/1d basis orbital basis set which was contracted 2,3/1,4/0,1. The Perdew-Zunger<sup>10</sup> LDF was used. During the self-consistent-field (SCF) process each one-electron energy level was exponentially broadened by 0.025 eV and then occupied from the lowest energy up to a single self-consistent Fermi energy,  $\epsilon_F$ , for both spins<sup>4</sup>.

The number of unpaired spins as a function of the distance between the two symmetry-inequivalent atoms in the  $I_h$   $Fe_{13}$  cluster is plotted in Fig. 1 and compared with similar curves for two less stable  $Fe_{13}$  structures. The  $O_h$  structure is the cuboctahedron, which is a compact portion of the fcc crystal lattice. The  $D_{3h}$  structure can be obtained from the fcc cluster by rotating any triad of nearest-neighbor surface atoms by  $60^\circ$  about their center. This third cluster is a compact portion of the hcp lattice. Each surface atom of the hcp and fcc clusters sees an identical nearest-neighbor environment. Therefore these two less stable clusters would be expected to have similar properties. Furthermore, these three clusters have the same equilibrium radial bond distance of  $4.4 \text{ bohr}^2$ . Nevertheless, Fig. 1 shows that these three clusters have quite different spin properties. For most radial bond distances the cluster magnetic moments are related,

$$\mu_{I_h} \geq \mu_{O_h} \geq \mu_{D_{3h}}. \quad (1)$$

This difference has been attributed to different symmetry-required degeneracy in these clusters<sup>3</sup>. The average degeneracy of an irreducible representation (IR) of the icosahedral ( $I_h$ ), octahedral ( $O_h$ ), and  $D_{3h}$  point groups are 3.2, 2, and  $1\frac{1}{3}$ , respectively. Furthermore, the maximal degeneracy of IRs of these groups are 5, 3 and 2, respectively. The optimal spin for each cluster changes quite abruptly as a function of radial bond distance for these three clusters because the room-temperature level-broadening parameter is small compared to the average spacing between the one-electron energy levels of at least one spin. For example a jump of 10 units between 4.5 and 4.6 bohr is required for the  $I_h$  cluster because the highest occupied molecular orbital (HOMO) and lowest unoccupied orbital (LUMO) have opposite spin,  $h_g$  and  $h_u$  orbital symmetry, and reverse their order in energy as the radial bond distance changes from 4.5 to 4.6 bohr. Beyond the plateau reached at largest bond distances

in this figure, the spin-polarized core  $d$  electrons reduce their overlap and ferromagnetic ordering may cease.

$\text{Fe}_{13}$  deviates slightly from perfect  $I_h$  geometry through the Jahn-Teller mechanism. The HOMO of minority spin is a five-fold degenerate  $h_u$  orbital that is occupied by only a single electron. If the symmetry unique central atom is removed, an icosahedral shell of 12 iron symmetry-equivalent atoms remains. This  $I_h$  shell has 38 unpaired spins and a radial bond distance of 4.2 bohr, yielding a radial contraction of 0.2 bohr upon removal of the central atom. Thus the net spin of the central atom is opposite that of the shell. This and other comparisons are made in Table 1, where the binding energy is defined as the total energy of the 13-atom cluster minus the energy of the shell and an isolated central atom. These energies are computed in (spatial) symmetry-restricted fashion<sup>11</sup>.

The size of the hole left inside a  $I_h$ -symmetric  $\text{Fe}_{12}$  shell can be computed two ways—using Slater atomic radii or the shell nearest-neighbor distance. The Slater atomic radius<sup>12</sup> for iron is 1.40Å (2.65 bohr), leaving a hole of radius 0.82Å (1.55 bohr) vacant in the center of the  $\text{Fe}_{12}$  shell. The nearest-neighbor distance of two atoms in the spherical shell is 105.15% of its radius. Subtracting half of this nearest-neighbor distance from the shell radius yields a hole radius of 1.05Å (1.99 bohr). The small size of this central hole and the fact that the shell lacks two electrons from having completely filled or half-filled shells suggest investigating divalent atoms that are smaller than iron as interesting candidates for filling that hole. Table 1 is heavily weighted with such atoms. From this table, the energetically most favorable such atom is zinc, the cluster containing which has 40 unpaired spins. Indeed it is the most stable cluster found in this study. The highest spin system found is  $\text{Fe}_{12}\text{S}$ , but it is energetically less stable than  $\text{Fe}_{12}\text{Zn}$ , although more stable than the pure  $\text{Fe}_{13}$  cluster. If  $\text{Fe}_{12}\text{O}$  has a slightly larger radial bond distance it too would have 44 unpaired spins and be stable against the Jahn-Teller mechanism. Interesting

semiclosed-shell nondivalent systems are  $\text{Fe}_{12}\text{Al}$  and  $\text{Fe}_{12}\text{Mn}$ . The former has high spin, 41 unpaired spins, and the latter has low spin, 35 unpaired spins.

Clearly these 13-atom  $I_h$  systems are rich in their magnetic properties and thus could potentially be tailored for engineering applications. Larger highly symmetric systems would afford greater flexibility. Studies of larger systems, specifically the  $\text{Fe}_{55} I_h$  and  $\text{Fe}_{51} O_h$  (bcc) clusters, are under way.

With larger magnetic systems the problem of double SCF convergence (simultaneously optimizing the one-electron orbitals and the number of unpaired spins) looms larger. A possible simplification in this effort is to change from using a spin unrestricted (ULDF) formulation of the problem to a restricted open-shell (ROLDF) formulation. Rather than direct optimization of the ROLDF problem, which in general leads to off-diagonal entries in the one-electron eigenvalue matrix,  $\epsilon$ , an average of the local potentials for both spins weighted by the number electron for each spin was used,

$$\epsilon_i \phi_i(\mathbf{r}) = \left[ -\frac{1}{2} \nabla^2 + \frac{N_\uparrow V_\uparrow(\mathbf{r}) + N_\downarrow V_\downarrow(\mathbf{r})}{N_\uparrow + N_\downarrow} \right] \phi_i(\mathbf{r}), \quad (2)$$

where the arrow subscripts denote the two spins and  $N$  and  $V(\mathbf{r})$  are the number of electrons and local potential. For  $\text{Fe}_{13}$  the two methods yield the same ordering of the one-electron levels and thus the same number of unpaired spins. For  $I_h \text{Fe}_{55}$ , with the nearest-neighbor distance between shells fixed at 4.4 bohr (the optimal distance for  $\text{Fe}_{13}$ , but likely too short for larger systems, thus underestimating their magnetic moments) Figs. 2 and 3 give the ROLDF and ULDF eigenvalue spectra. Both calculations yield the same number of unpaired electrons, 64, but the spectra and level ordering are slightly different. The ROLDF approximation does not significantly improve the SCF process, despite stabilizing the orbitals of minority spin near the Fermi energy. Nevertheless, because more than a hundred iterations are needed to reach

an acceptable level of convergence, the ROLDF saves almost a third of the computer time.

Symmetry can have a significant effect on the magnetic moments of small clusters. Currently this effect is most easily addressed theoretically; thus it is important to extend theoretical methods to reliably and economically treat larger clusters.

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These calculations were made using a grant of CRAY X-MP computer time from the Naval Research Laboratory. This work was supported in part by the Office of Naval Research through contract number N0001490WX24264.

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TABLE

Table 1. Stability, size, and magnetic moments for selected central atoms in an icosahedral  $\text{Fe}_{12}\text{X}$  cluster. The binding energy is in hartrees and radial bond distance in bohr. An up arrow subscript on the highest open-shell spin-orbital indicates that it is occupied by majority-spin electrons.

Central atom	Binding energy	Radial bond distance	Unpaired electrons	Open-shell electrons	Open-shell orbital
None	0.000	4.2	38	3	$h_{g\uparrow}$
Be	0.178	4.3	40	0	—
O	0.118	4.3	42	4	$h_{g\uparrow}$
Mg	0.010	4.5	40	0	—
Al	0.145	4.4	41	0	—
Si	0.258	4.4	40	0	—
S	0.053	4.5	44	0	—
Ti	0.262	4.5	38	2	$h_{g\downarrow}$
Mn	0.206	4.5	35	0	—
Fe	0.006	4.4	34	1	$h_{u\downarrow}$
Ni	0.211	4.4	38	3	$h_{g\uparrow}$
Zn	0.372	4.4	40	0	—
Se	-0.046	4.6	38	3	$h_{u\downarrow}$
Pd	0.109	4.6	38	3	$h_{g\uparrow}$

## FIGURE CAPTIONS

*Figure 1* The optimal number of unpaired spins as a function of radial bond distance for the hcp (long-dashed curve), fcc (solid curve), and  $I_h$  (short-dashed curve)  $Fe_{13}$  clusters.

*Figure 2* Comparison between the a) restricted open-shell and b) unrestricted one-electron eigenvalue spectra for  $I_h$   $Fe_{55}$ . In each panel the majority-spin spectra are to the right of the minority-spin spectra. Both methods give the same number of unpaired electrons, 64, which is fixed by the large gap in the minority-spin spectra at the Fermi energies.

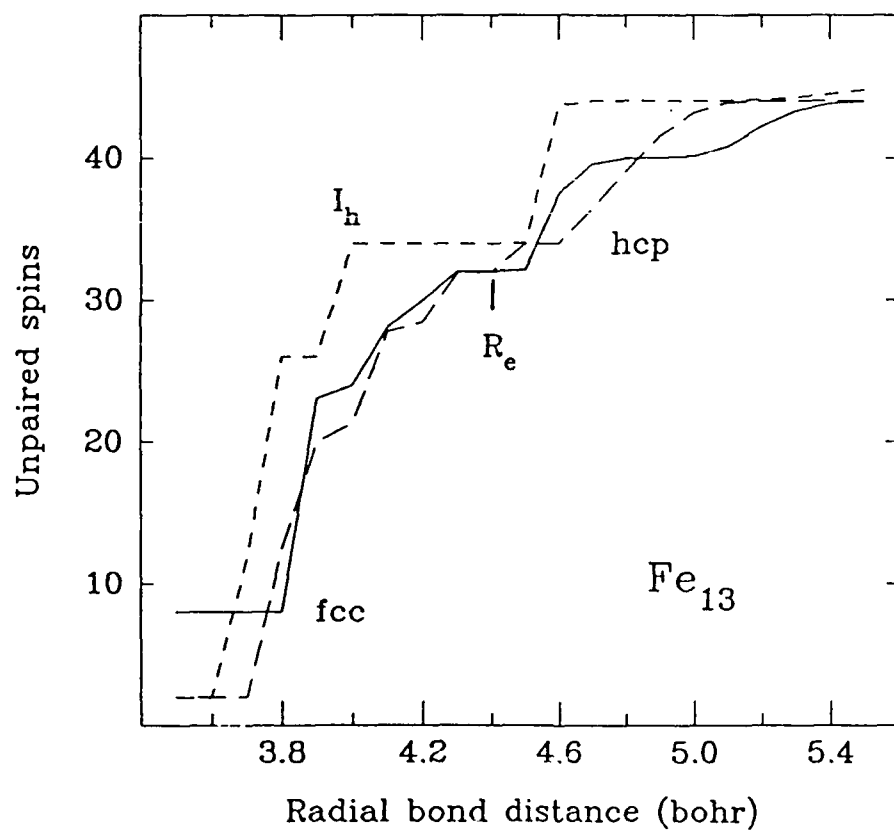
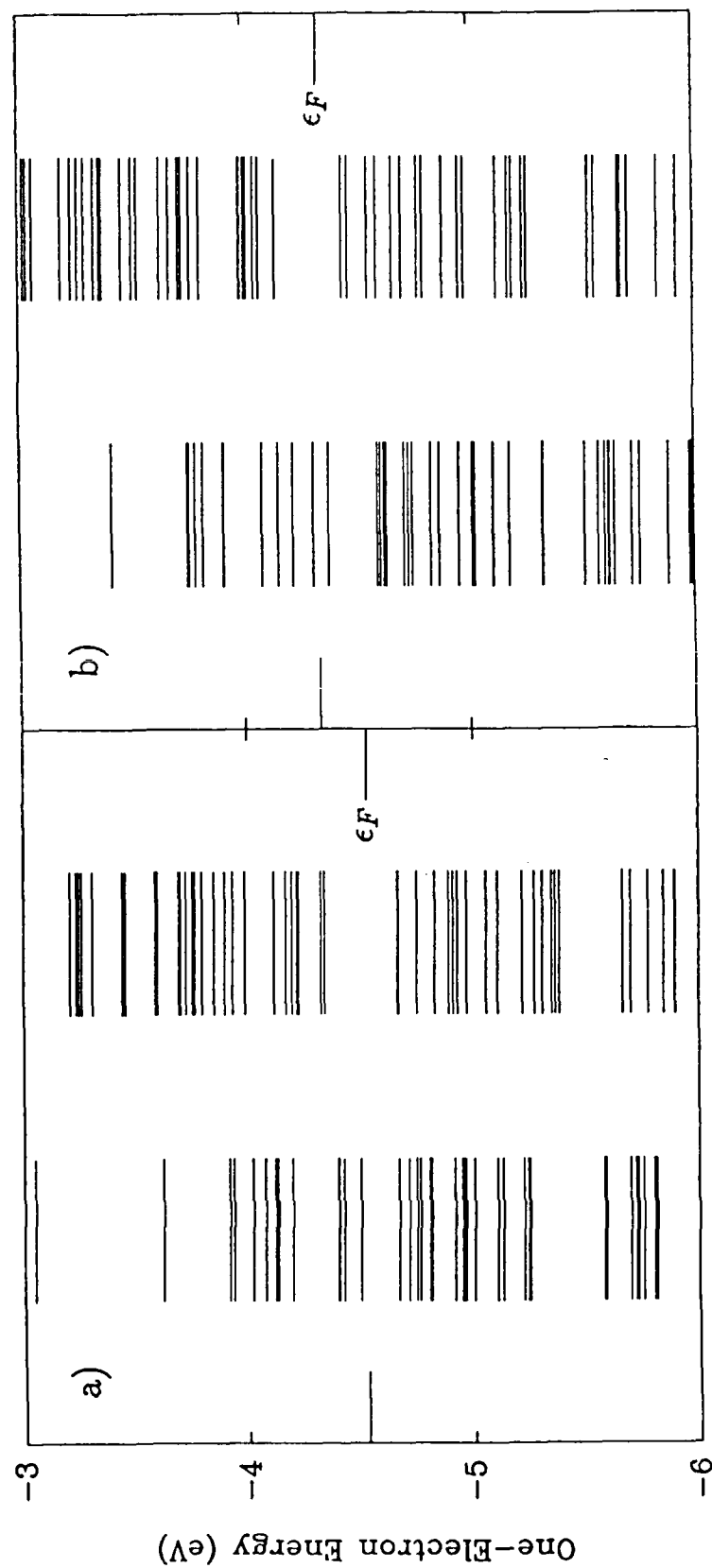


Fig. 1

ROLDF Icosahedral Fe<sub>55</sub>

ULDF Icosahedral Fe<sub>55</sub>



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